Supplementary Information

Benzoindolium-Triarylborane Conjugates: Ratiometric Fluorescent Chemodosimeter for the Detection of Cyanide ions in Aqueous Medium

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Cartesian coordinates for the calculated structure of **3, 3**-CN^- and **3**-B-CN^-

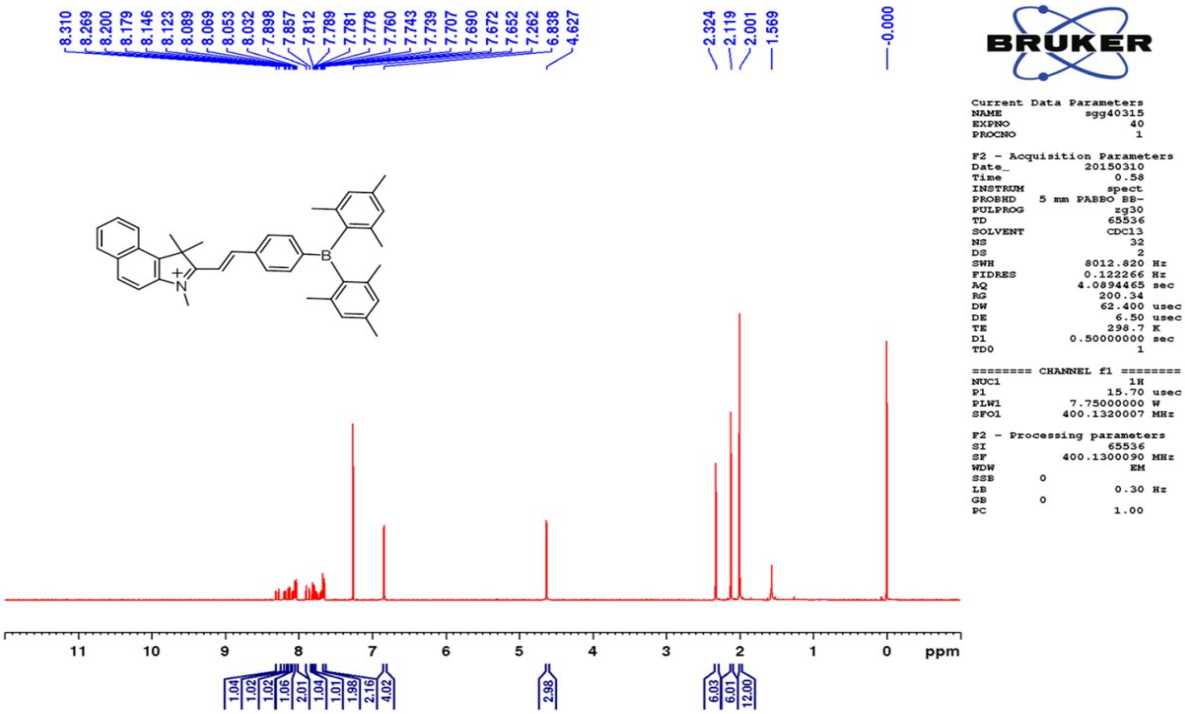


Fig. S1. ^{1}H NMR of **3** in $CDCl_3$

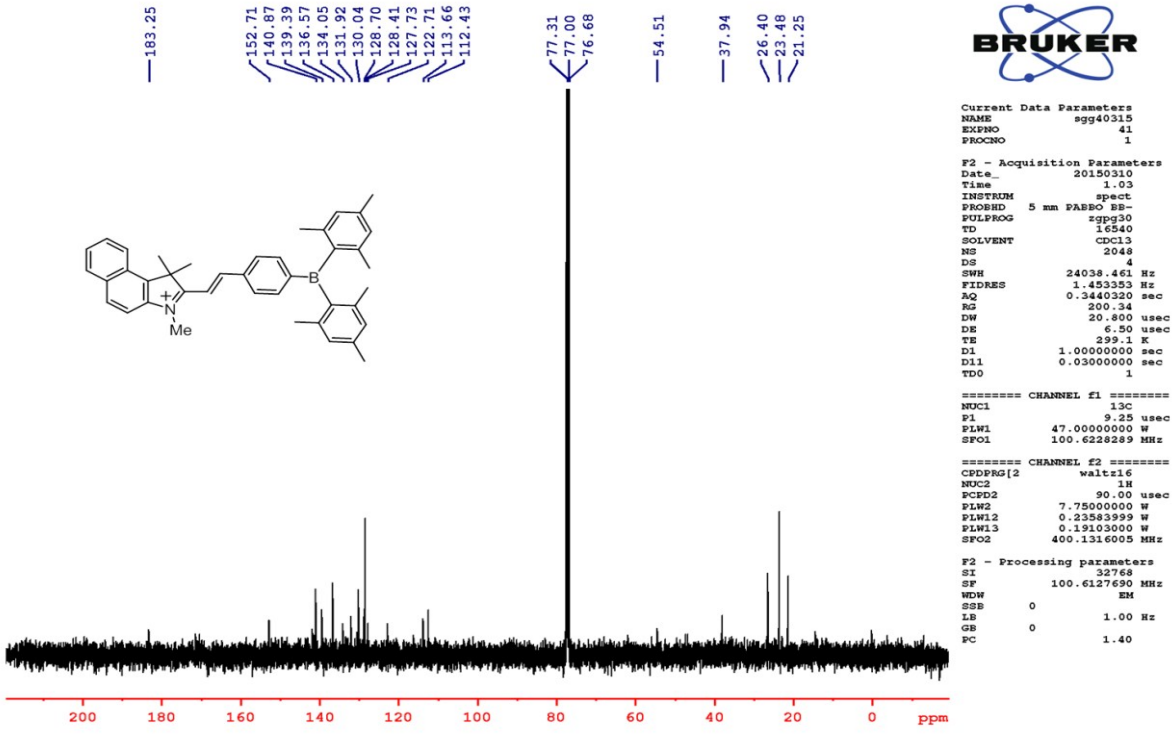


Fig. S2. $^{13}C\{^{1}H\}$ NMR of **3** in $CDCl_3$

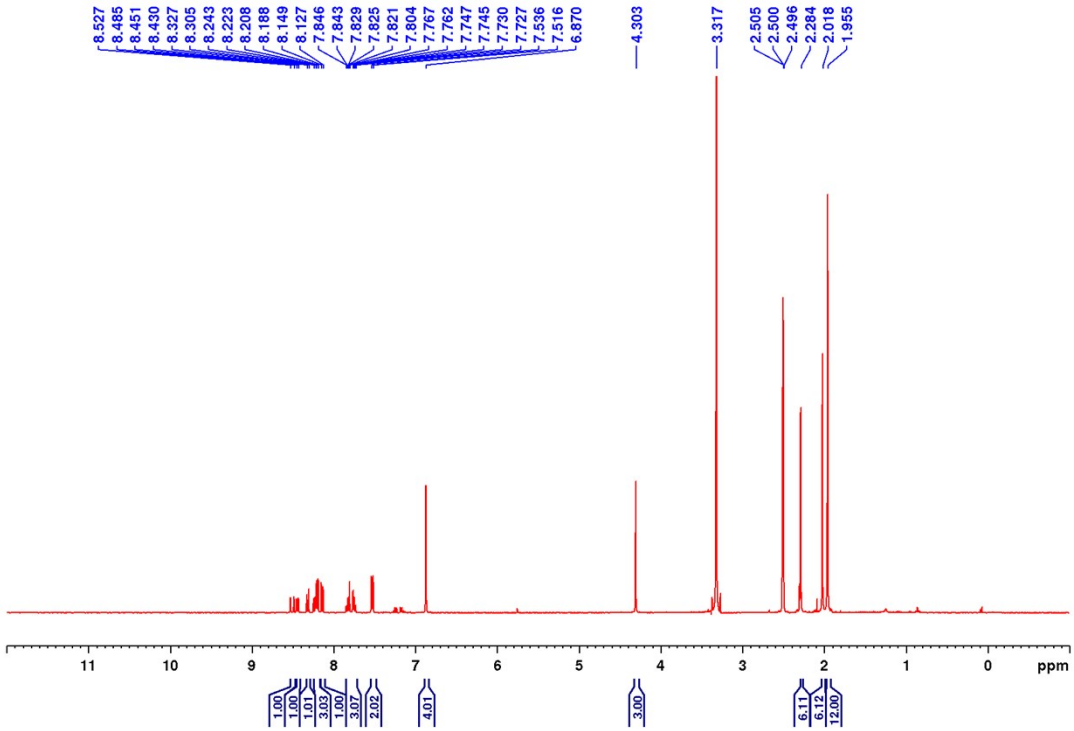


Fig. S3. ^{1}H NMR of **3** in d6-DMSO

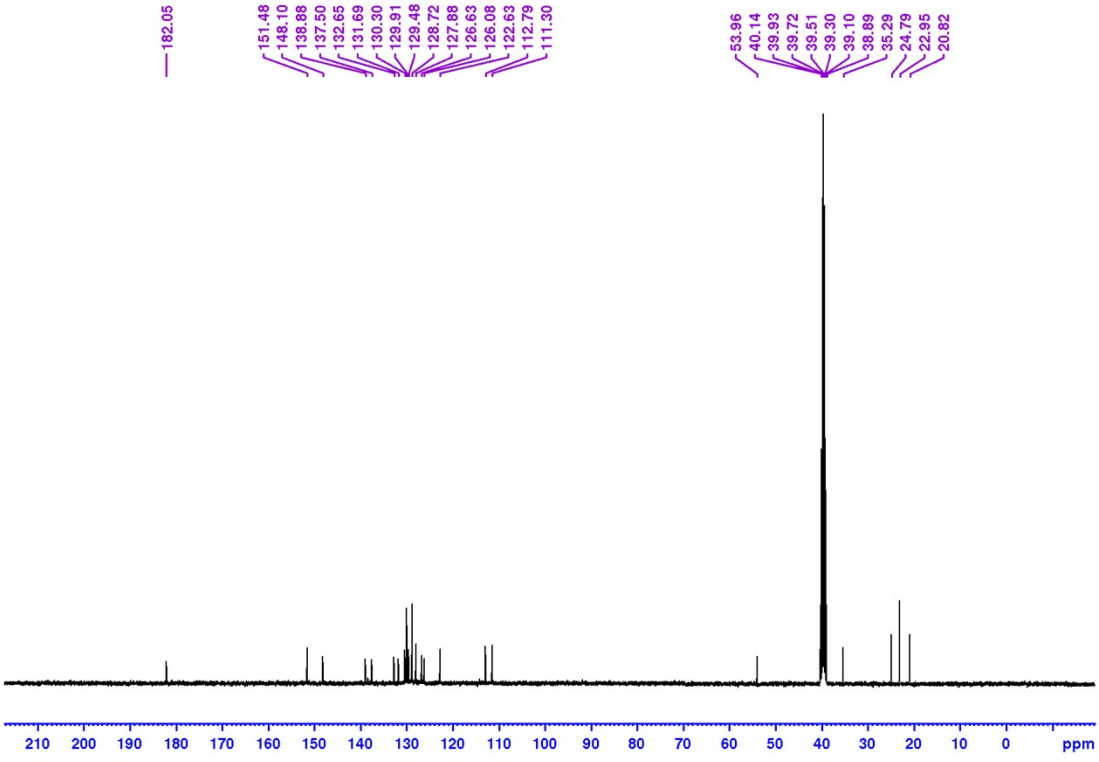


Fig. S4. ^{13}C{^{1}H} NMR of **3** in d6-DMSO

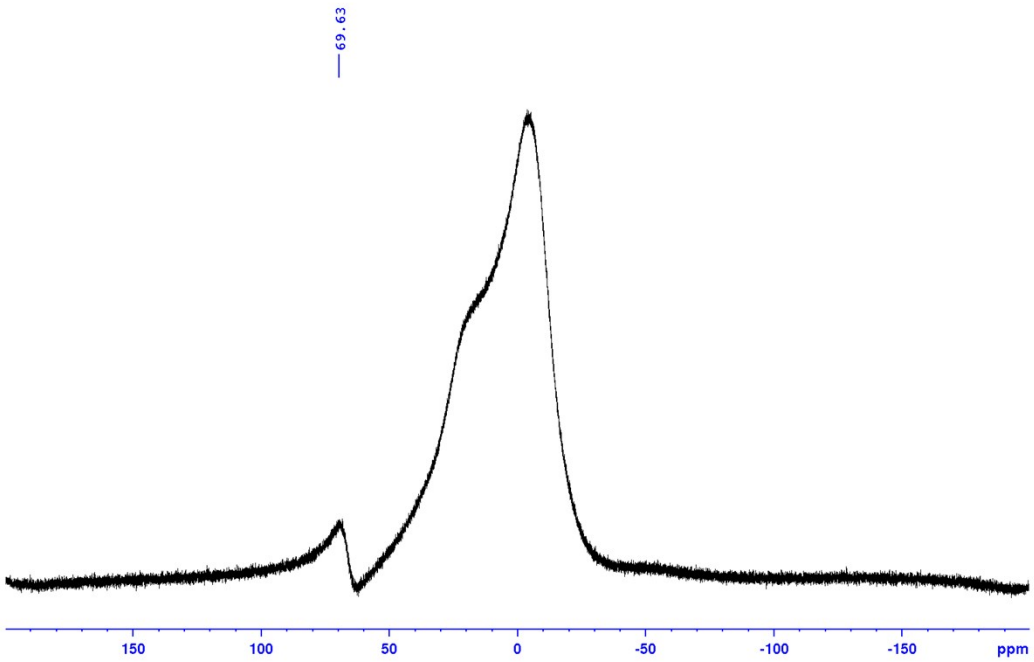


Fig. S5. ^{11}B NMR of 3 in d6-DMSO

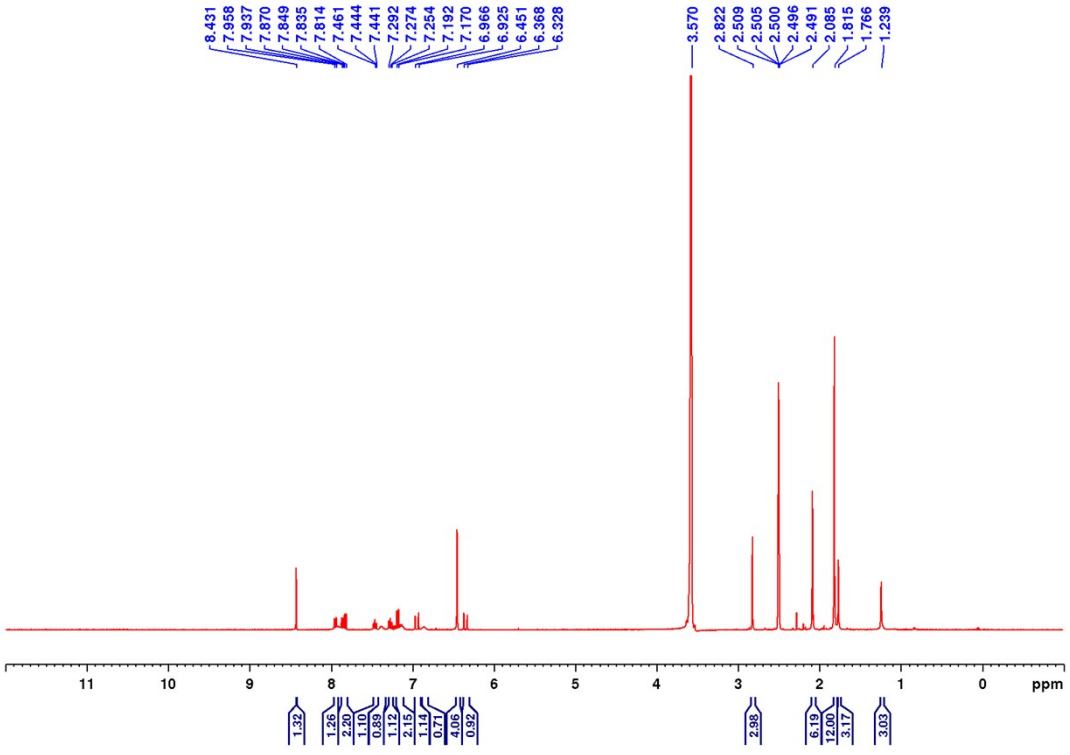


Fig. S6. ^{1}H NMR of **3**+NaCN in d6-DMSO:D_2O

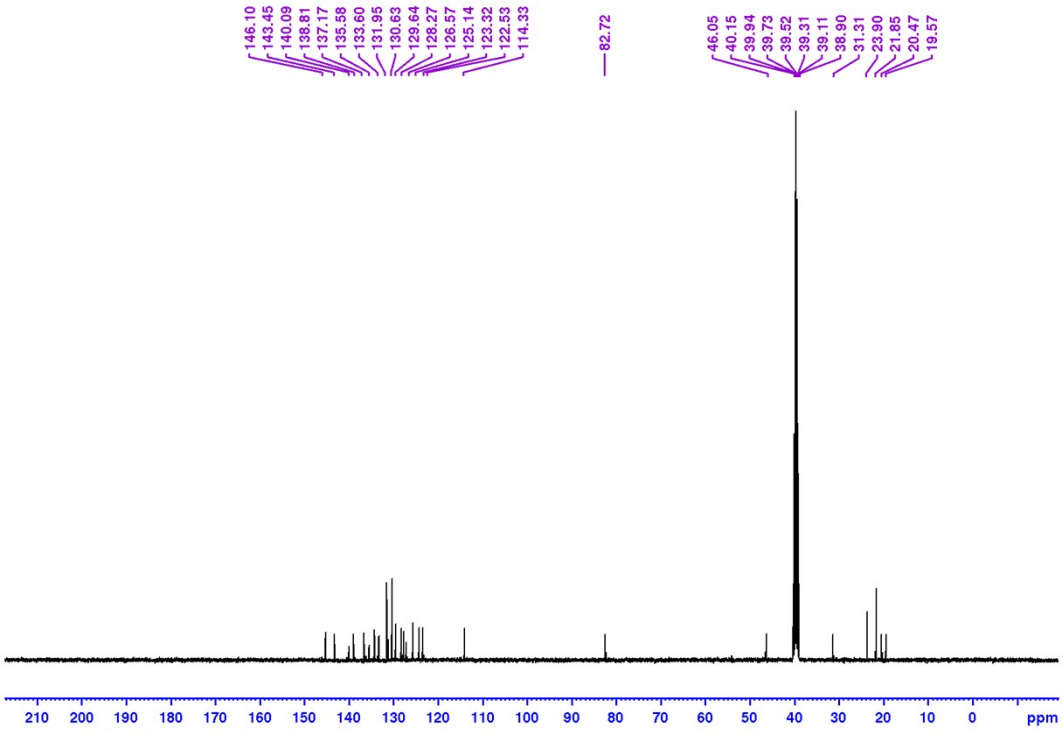


Fig. S6. $^{13}C\{^{1}H\}$ NMR of **3**+NaCN in d6-DMSO:D_2O

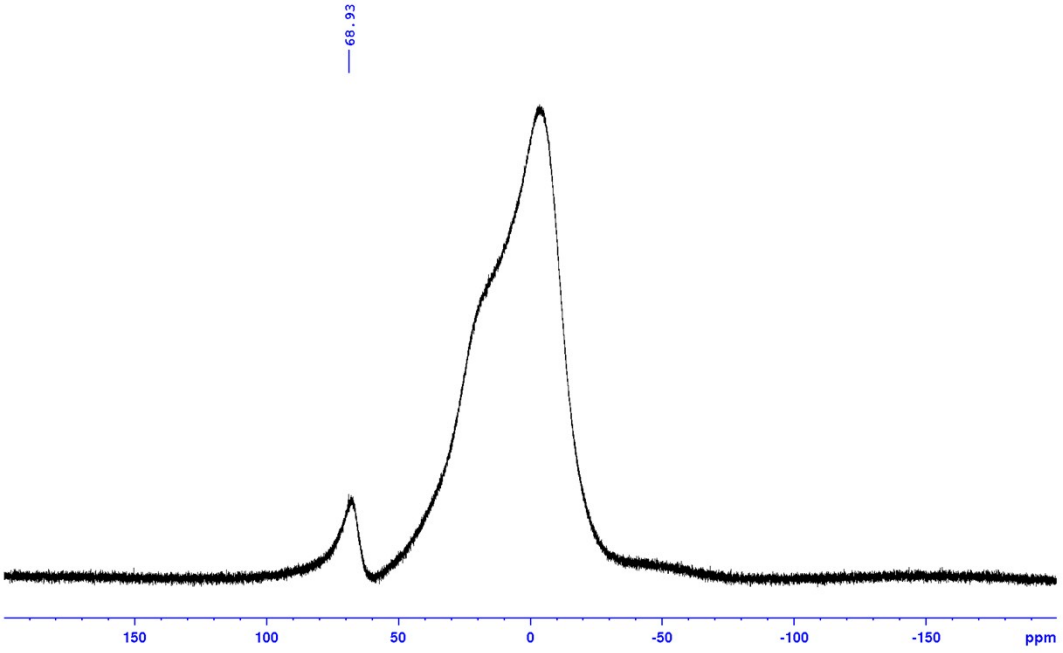


Fig. S8. ^{1}H NMR of **3**+NaCN in d6-DMSO:D_2O

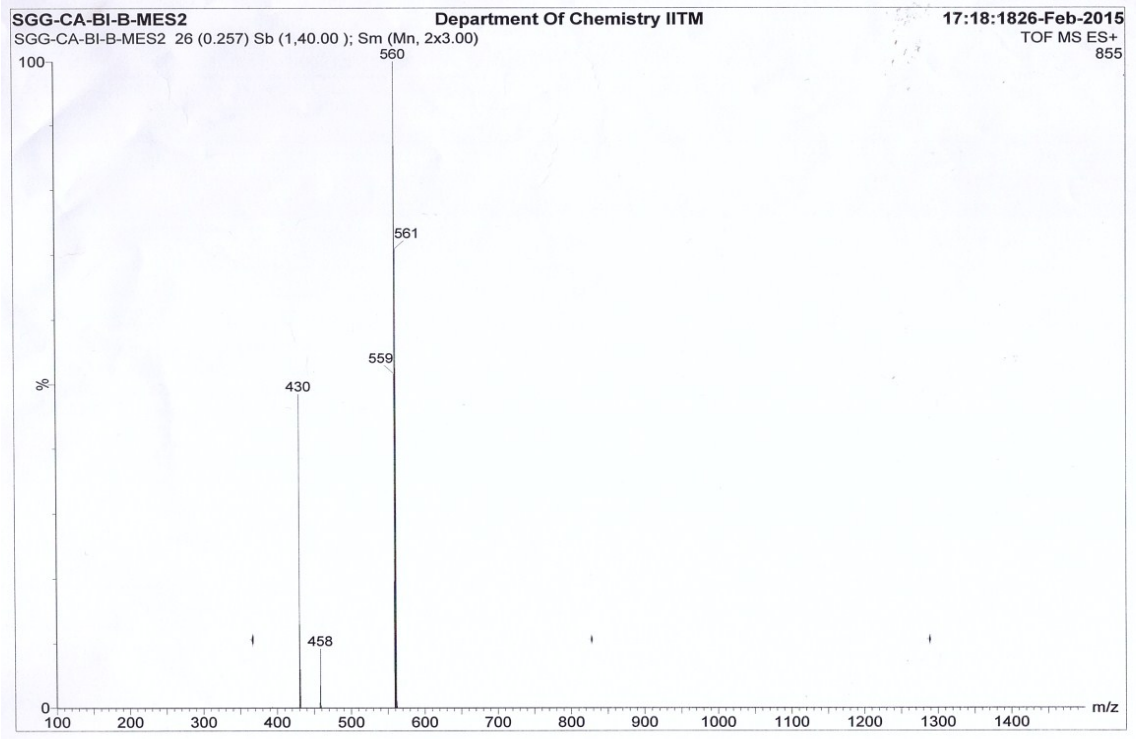


Fig. S9. ESI-MS spectrum of 3

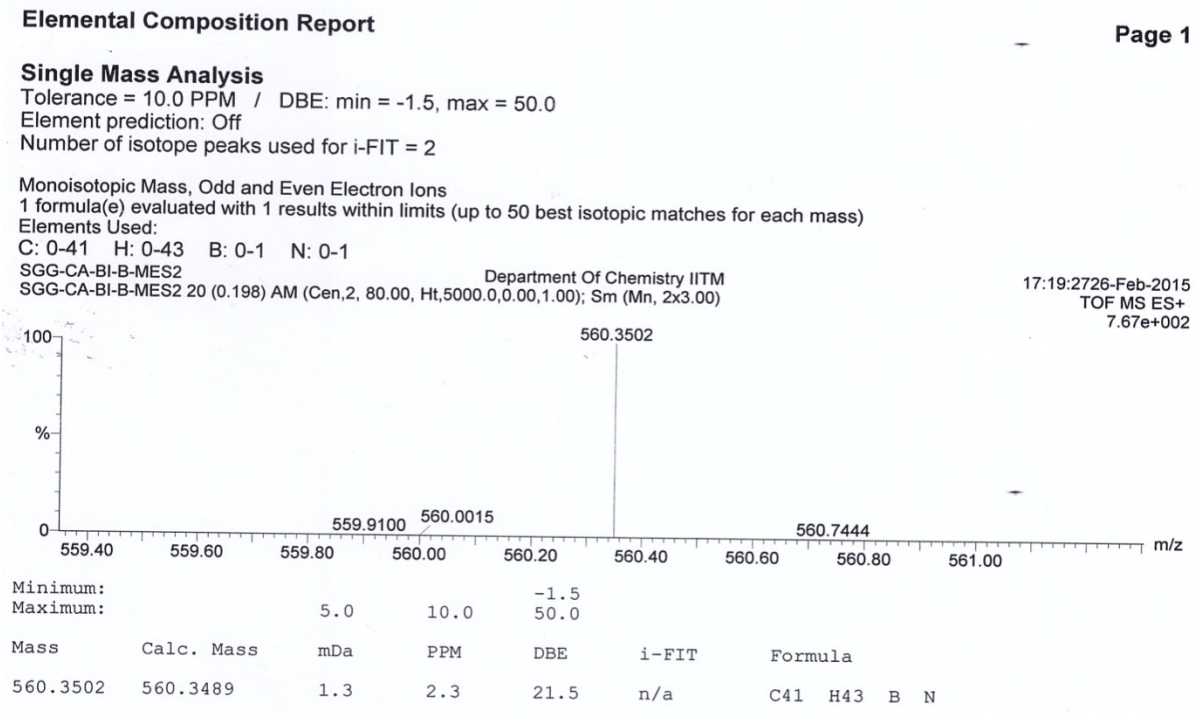


Fig. S10. HRMS spectrum of 3

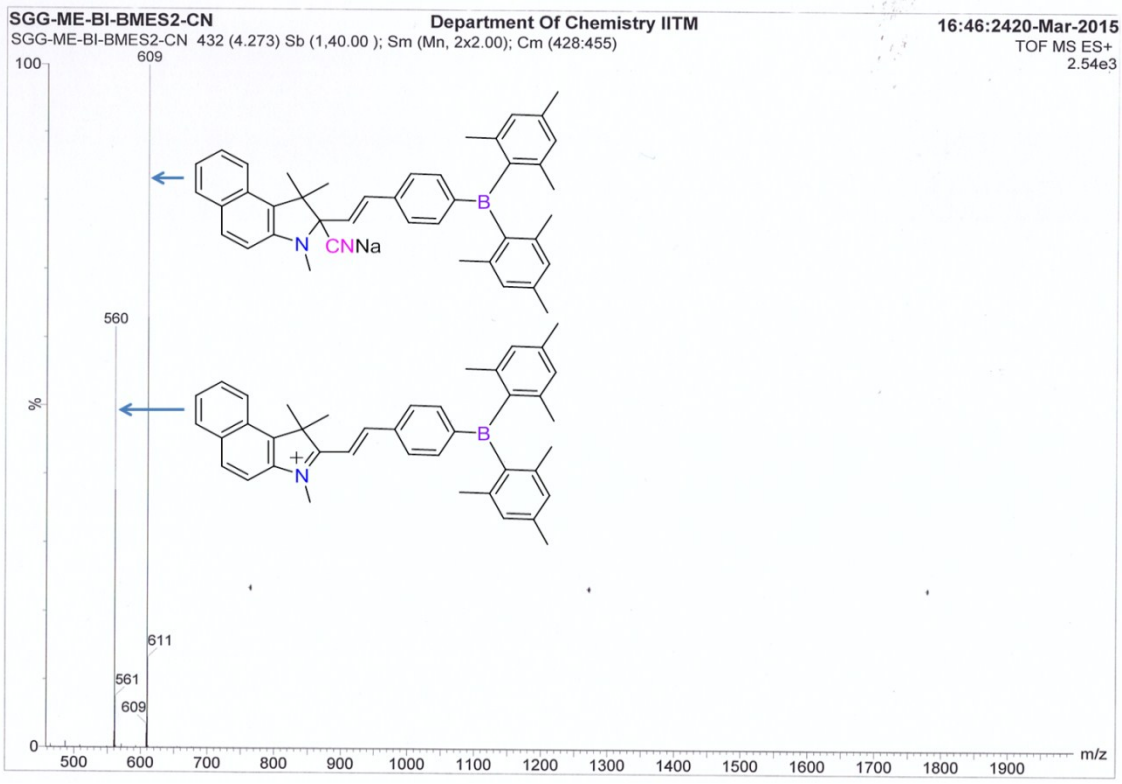


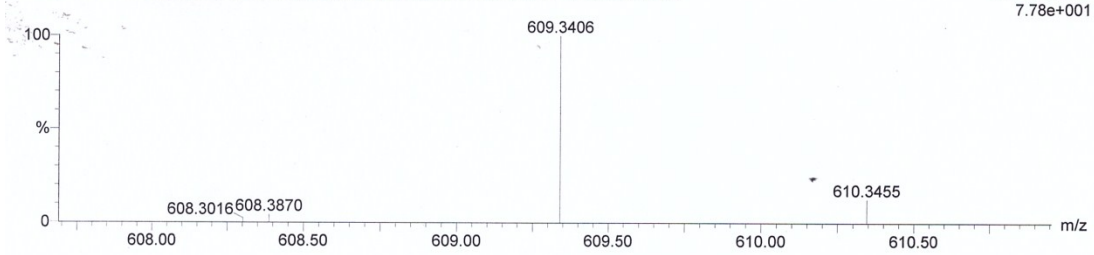
Fig. S11. ESI-MS spectrum of 3+CN$^-$

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Odd and Even Electron Ions
2 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-42 H: 0-43 B: 0-1 N: 0-2 Na: 0-1

SGG-ME-BI-BMES2-CN
Department Of Chemistry IITM
16:51:4920-Mar-2015
SGG-ME-BI-BMES2_CN 6 (0.059) AM (Cen,4, 80.00, Ht,5000.0,0.00,1.00); Sm (Mn, 2x2.00)
TOF MS ES+
7.78e+001



Minimum:				-1.5		
Maximum:		5.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
609.3406	609.3417	-1.1	-1.8	22.5	12.9	C42 H43 B N2 Na

Fig. S12. HRMS spectrum of 3+CN$^-$

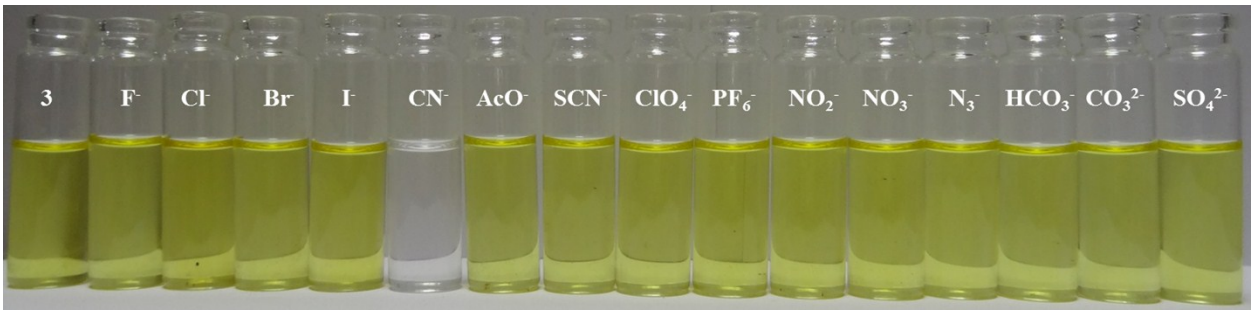


Fig. S13. Photographs of **3** in MeCN/water mixture (1:9) under day light in the presence of different anions.

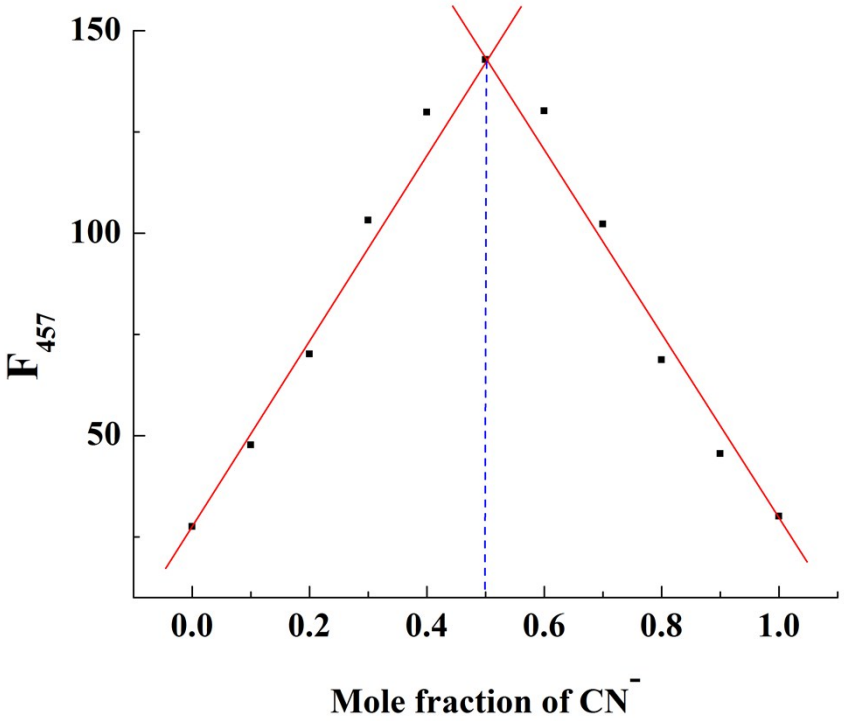


Fig. S14. Job's plot of **3** with CN^-anions in CH_3CN/water (1:9, v/v) indicating the formation of 1:1 complex.

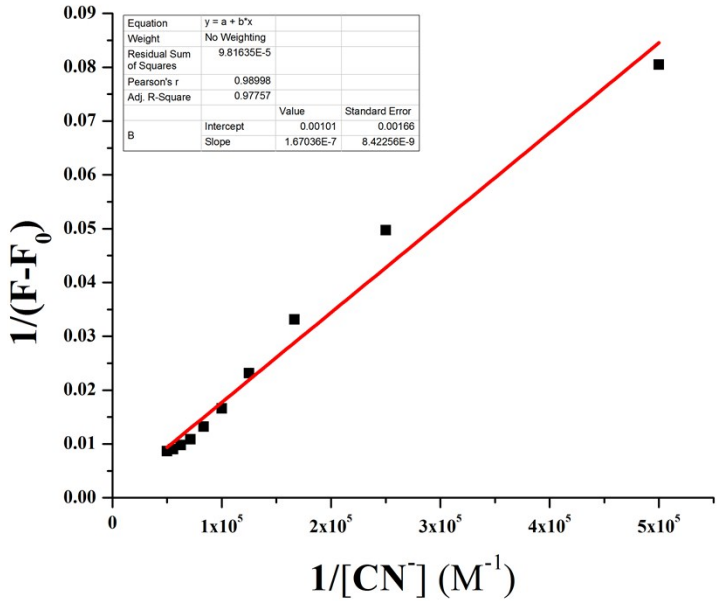


Fig. S15. Benesi-Hildebrand plot obtained from the emission spectrum (fluorescence calculated from 457 nm) for **3**-CN^-

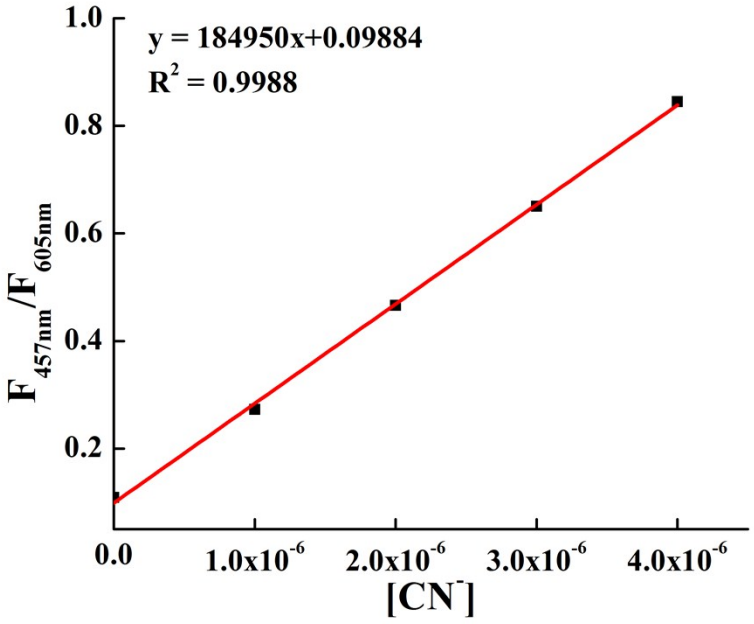


Fig. S16. Linear response in fluorescence ratio intensity of probe **3** in the presence of increasing CN^- concentrations.

Single-Crystal X-ray Diffraction:

X-ray diffraction data for the crystal **3** was collected using Bruker Kappa apexII CCD single crystal diffractometer, equipped with graphite monochromated MoKα (λ=0.71078Å) radiation. Data collection was carried out at 296K using ω-φ scan modes. The collected frames were integrated followed by Lorentz and Polarization correction using the program SAINT-APEXII[1]. Multi-scan absorption correction has been employed for the data using SADABS[1] program. The molecular structure was solved by direct methods procedure using SHELXS-2012[2]. Initially isotropic refinements of non-hydrogen atoms were carried out followed by full-matrix least squares refinement with anisotropic thermal parameters for non-hydrogen atoms through SHELX-2012[2] program. The hydrogen atoms associated with the carbon atoms were identified from the difference electron density map and were allowed to ride on the parent atom using suitable constraint, with distance 0.93Å(for aromatic CH) and 0.96Å(CH3) and thermal displacement of Ueq(H) = 1.2Uiso(C) and Ueq(H) = 1.5Uiso(C) respectively. The structural parameters for **3** have been listed in Table S1.

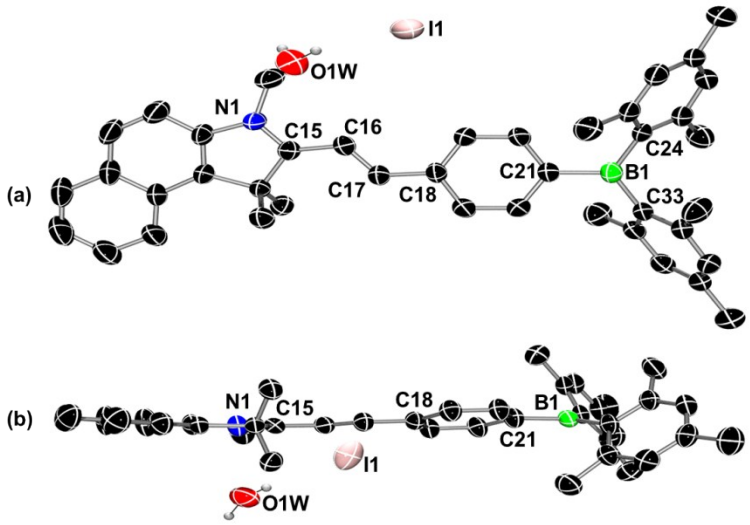
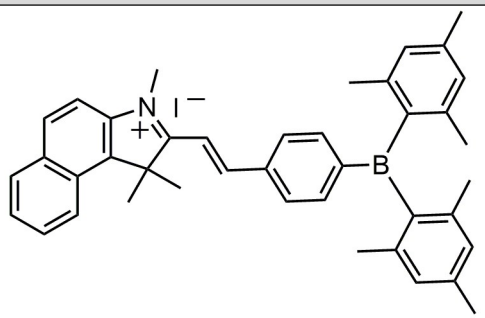
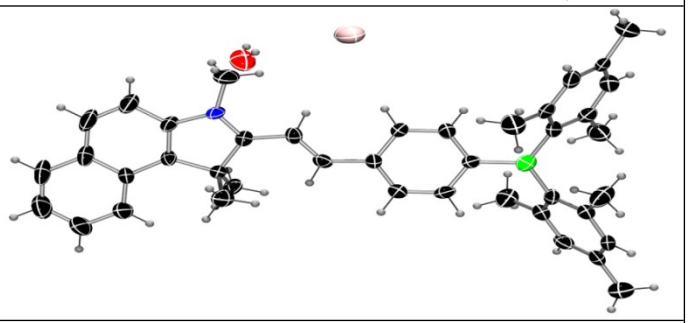


Fig. S17. Molecular structure of **3.** (50% probability for thermal ellipsoids). a) Front view b) side view. Except water molecule hydrogen atoms are not shown for clarity.

Table S1. Crystallographic Data and Structure Refinements Summary for Compound **3:**

Data	**3**
Molecular structure	
ORTEP structure	
Formula	$C_{41}H_{44}BINO_{0.50}$
Formula weight	696.48
Color	red
Crystal morphology	block
Temperature/K	296(2)
Radiation	Mo Kα
Wavelengh/Å	0.71073
Crystal system	Monoclinic
Space group	P21/c
a (Å)	23.094(3)
b (Å)	9.7806(12)
c (Å)	15.9792(18)
α (°)	90
β (°)	94.232(3)
γ (°)	90
Volume ($Å^3$)	3599.4(3)
Z	4
Density (g/ml)	1.285
μ (1/mm)	0.919
F (000)	1436
θ (min, max)	1.768, 26.370
No. of unique reflns	7315
No. of parameters	432
R_obs, wR2_obs	0.0473, 0.1096

GooF	1.006

Computational details:

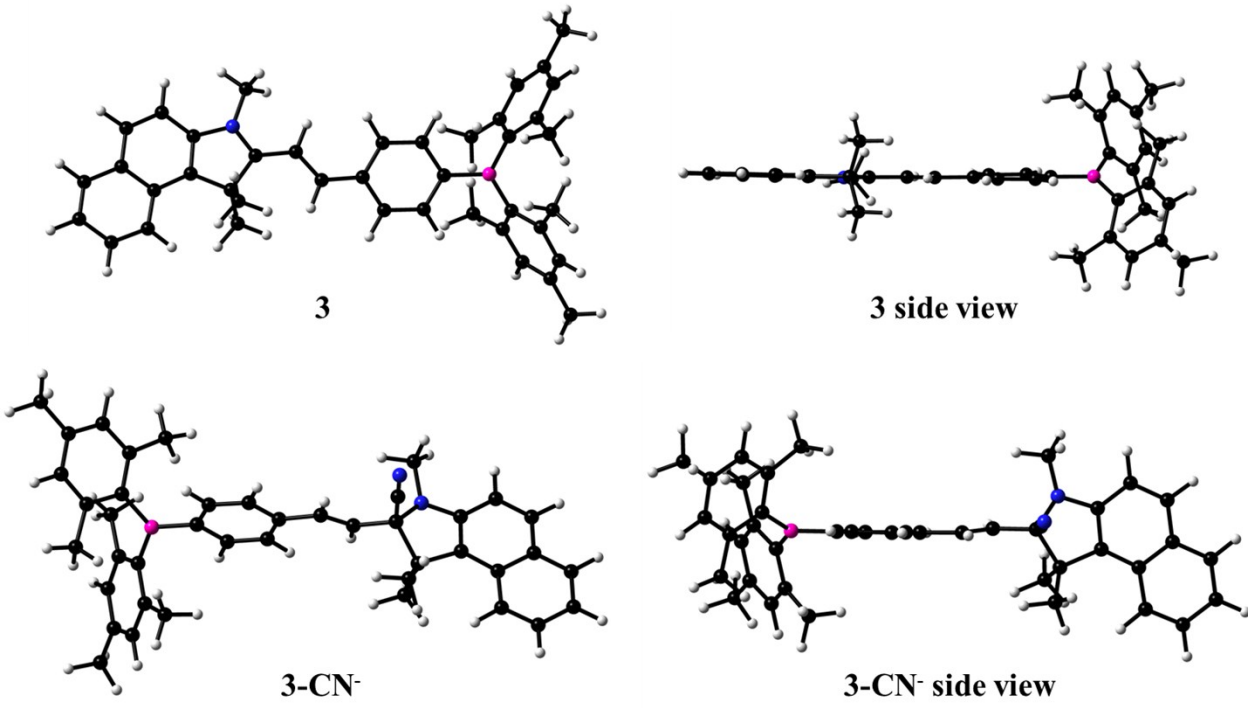


Fig. S18. Optimized geometries of **3** and **3**-CN^-

Table S2. HOMO-LUMO energy calculated for species **3** and **3**-CN^-

Species	E(HOMO)	E(LUMO)	ΔE (Hartree)	ΔE (eV)
3	-0.2871	-0.21657	0.07053	1.919234148
3-CN^-	-0.19224	-0.07375	0.11849	3.224302484

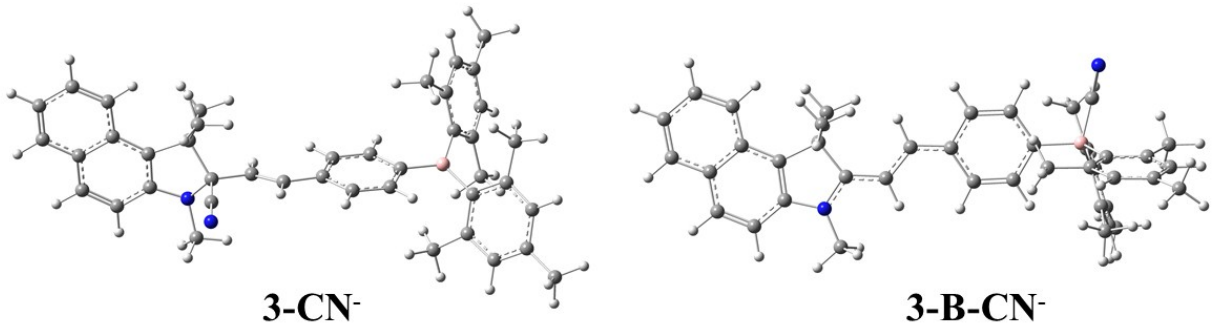


Fig. S19. Optimized structure of cyanide adducts at different binding sites (**3**-CN^- and **3**-B-CN^-) and energy comparison of the optimized structures of **3**-CN^- and **3**-B-CN^-.

Table S3. Selected electronic excitation energies (eV), oscillator strengths (f), major contributions of low-lying excited states of the probe **3** and **3**-CN^- at the CAM-B3LYP/6-31G(d) level in water.

Compound	Electronic Transition	Excitation Energy (nm, eV)	Oscilator Strength (*f*)	Major Contribution
3	S0→S1	423.7 (2.92)	1.3117	HOMO→LUMO (88%)
	S0→S2	347.5 (3.56)	0.0847	H-1→LUMO (71%) H-1→L+1 (22%)
	S0→S3	336.9 (3.68)	0.3192	H-5→LUMO (33%) H-2→LUMO (37%)
	S0→S4	317.9 (3.90)	0.0598	H-5→LUMO (38%) H-2→LUMO (36%) H-2→L+1 (13%)
	S0→S5	309.0 (4.01)	0.0212	H-7→LUMO (45%) H-3→LUMO (40%)
3-CN^-	S0→S1	309.8 (4.00)	0.1355	H-2→LUMO (27%) H-1→LUMO (59%)
	S0→S2	307.4 (4.03)	0.2664	HOMO→L+1 (71%)
	S0→S3	304.7 (4.06)	0.6098	H-2→LUMO (51%) H-1→LUMO (23%) HOMO→L+1 (15%)
	S0→S4	286.5 (4.32)	0.0007	HOMO→LUMO (73%) HOMO→L+2 (11%)
	S0→S5	276.7 (4.48)	0.2006	H-4→LUMO (80%)

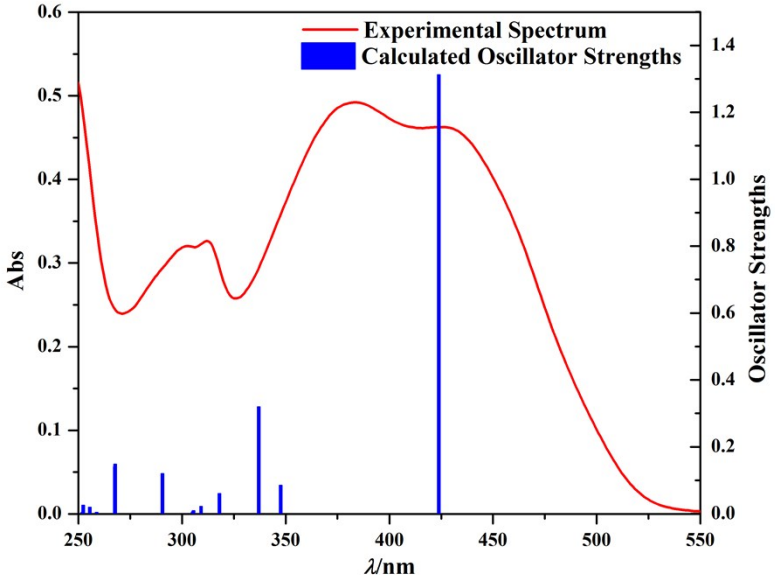


Fig. S20. Comparison between the experimental UV-visible absorption spectrum of **3** in MeCN/water mixture (1:9, v/v) and TD-DFT (CAM-B3LYP/6-31G(d)) calculated transitions of compound **3** from the optimized (B3LYP/6-31G(d)) ground state structure.

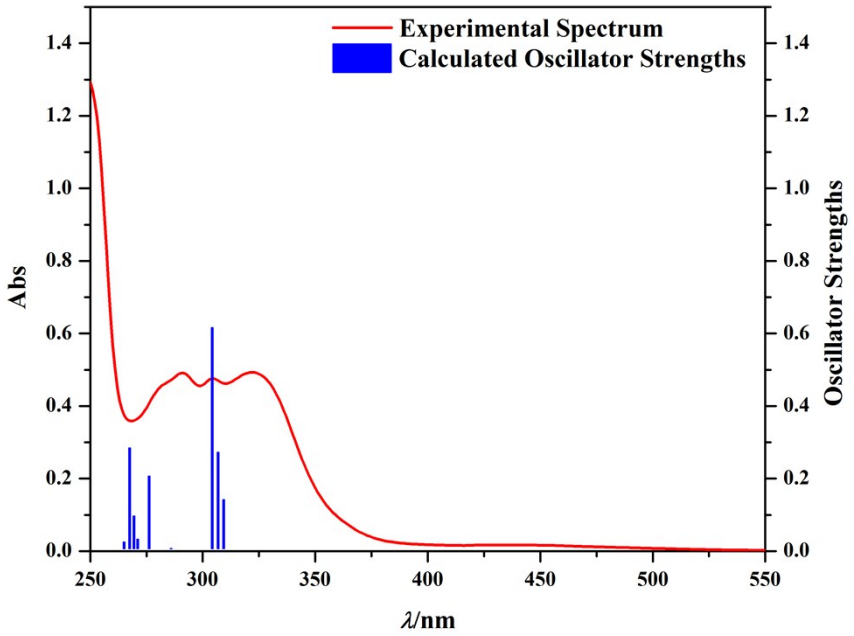


Fig. S21. Comparison between the experimental UV-visible absorption spectrum of **3**-CN^- in MeCN/water mixture (1:9, v/v) and TD-DFT (CAM-B3LYP/6-31G(d)) calculated transitions of compound **3**-CN^- from the optimized (B3LYP/6-31G(d)) ground state structure.

References:

1. Bruker (2004). APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.

2. Sheldrick, G. M, Acta Cryst. 2015, **C71**, 3.

Cartesian coordinates for the calculated structure of 3

Energy = -1667.72421690 a. u.

C	10.240072000	1.340823000	0.911183000	H	10.909662000	-0.385950000	-0.165309000
C	10.055074000	0.189581000	0.180029000	H	7.003813000	2.256379000	1.421336000
C	8.751697000	-0.271539000	-0.139014000	H	9.273332000	2.989720000	1.932088000
C	7.608025000	0.481163000	0.312620000	H	9.452605000	-2.010665000	-1.215704000
C	7.840095000	1.666242000	1.065967000	H	7.213353000	-2.852539000	-1.790517000
C	9.120808000	2.082104000	1.355669000	H	5.353950000	1.183348000	2.301221000
C	8.571029000	-1.464071000	-0.893652000	H	3.640583000	0.840293000	2.030670000
C	7.322210000	-1.937467000	-1.219959000	H	4.794261000	-0.489968000	2.230322000
C	6.216545000	-1.186725000	-0.772784000	H	4.849960000	1.834988000	-1.464400000
C	6.324997000	-0.024077000	-0.032044000	H	5.397275000	2.612286000	0.023968000
N	4.840888000	-1.472559000	-0.986698000	H	3.680869000	2.253989000	-0.200395000
C	4.049657000	-0.562389000	-0.406718000	H	2.241380000	-1.540668000	-0.973722000
C	4.924778000	0.495733000	0.273700000	H	2.122208000	1.101022000	0.580774000
C	4.656093000	0.507620000	1.802601000	H	3.658675000	-2.310340000	-2.514308000
C	4.692538000	1.884048000	-0.382723000	H	5.210746000	-3.110858000	-2.235215000
C	2.635859000	-0.669715000	-0.462036000	H	3.884078000	-3.352763000	-1.079059000
C	1.739348000	0.220602000	0.074653000	C	0.301788000	0.131003000	0.042896000
C	4.365711000	-2.632086000	-1.746415000	C	-0.444574000	1.186318000	0.617897000
H	11.242620000	1.682945000	1.148690000	C	-0.407633000	-0.952418000	-0.529209000

C	-1.831908000	1.168650000	0.602100000
H	0.082367000	2.026420000	1.064792000
C	-1.792016000	-0.971440000	-0.510740000
H	0.128018000	-1.786112000	-0.973938000
C	-2.546946000	0.088823000	0.044402000
H	-2.381830000	2.003038000	1.027839000
H	-2.317891000	-1.823569000	-0.932101000
B	-4.138879000	0.059479000	0.042076000
C	-4.846028000	-1.338503000	0.183819000
C	-5.822198000	-1.753042000	-0.767371000
C	-4.519245000	-2.235210000	1.236888000
C	-6.402578000	-3.019394000	-0.663363000
C	-5.151270000	-3.479272000	1.322398000
C	-6.090833000	-3.898176000	0.378507000
H	-7.129650000	-3.326084000	-1.412787000
H	-4.906575000	-4.139172000	2.152737000
C	-4.901264000	1.426735000	-0.102215000
C	-5.922244000	1.787958000	0.825424000
C	-4.586658000	2.349774000	-1.136446000
C	-6.551159000	3.030262000	0.720587000
C	-5.267461000	3.567973000	-1.224013000
C	-6.243578000	3.938091000	-0.297670000
H	-7.315523000	3.294354000	1.448759000
H	-5.033175000	4.244912000	-2.043593000
C	-3.521685000	-1.886868000	2.327811000
H	-2.491589000	-2.117627000	2.028493000
H	-3.545700000	-0.827581000	2.602327000
H	-3.730517000	-2.462764000	3.235078000
C	-6.251971000	-0.875014000	-1.927105000
H	-5.403738000	-0.536197000	-2.533320000
H	-6.928068000	-1.421914000	-2.591138000
H	-6.774974000	0.023114000	-1.583387000
C	-6.773674000	-5.239425000	0.492956000
H	-6.219653000	-5.918180000	1.148982000
H	-7.784284000	-5.132846000	0.908639000
H	-6.878945000	-5.720352000	-0.485784000
C	-6.354255000	0.877679000	1.959076000
H	-6.825970000	-0.037673000	1.588037000
H	-5.514147000	0.568641000	2.591665000
H	-7.075812000	1.387706000	2.604308000
C	-3.555159000	2.060145000	-2.213271000
H	-2.554037000	2.400317000	-1.919614000

H	-3.475318000	0.995954000	-2.453301000	H	-6.533611000	5.979322000	0.352370000
H	-3.813926000	2.584316000	-3.139046000	H	-6.824924000	5.725630000	-1.372711000
C	-6.941713000	5.273320000	-0.383014000	H	-8.013353000	5.178753000	-0.175788000

Cartesian coordinates for the calculated structure of 3-CN$^-$

Energy = -1760.75047660 a. u.

C	7.285247800	-2.965652860	4.833863900	C	1.582225250	0.212500020	0.064289880
C	7.195660710	-3.752142260	3.707996610	C	4.187602440	-2.418737930	-2.055288980
C	6.501297200	-3.301531400	2.555598730	H	7.819422220	-3.322103360	5.709169710
C	5.882078320	-1.999661220	2.570472650	H	7.658181690	-4.735191710	3.685568040
C	5.996731060	-1.215987120	3.753058840	H	5.543601070	-0.232898440	3.799170170
C	6.679519490	-1.687930920	4.852223630	H	6.753830480	-1.072036330	5.743537810
C	6.412593140	-4.123054450	1.397374460	H	6.886187500	-5.100241450	1.419115470
C	5.748032300	-3.716040170	0.264754840	H	5.690335050	-4.364957790	-0.601455290
C	5.152047710	-2.439382990	0.296738090	H	3.538789040	-0.043442620	3.029445370
C	5.197691910	-1.596278750	1.391863560	H	2.636143220	0.754972050	1.735507350
N	4.420395260	-1.806466800	-0.744412360	H	2.544847080	-1.004022580	1.930522990
C	4.438229930	-0.317026350	1.058658110	H	6.219010930	0.774779940	0.382661550
C	3.210925500	-0.138143460	1.992251140	H	5.806541280	1.044152340	2.078625140
C	5.386581850	0.912790690	1.079245030	H	4.862753660	1.832602960	0.808831610
C	2.478736250	-0.677816980	-0.472399120	H	2.084257250	-1.548769980	-0.984085120

H	1.965085250	1.092920020	0.570410880
H	4.484413730	-1.727760150	-2.847458670
H	4.789186080	-3.320348900	-2.141469120
H	3.131958100	-2.681581140	-2.170346290
C	0.144665250	0.122901020	0.032532880
C	-0.601696750	1.178216020	0.607533880
C	-0.564755750	-0.960519980	-0.539572120
C	-1.989030750	1.160548020	0.591736880
H	-0.074755750	2.018318020	1.054428880
C	-1.949138750	-0.979541980	-0.521103120
H	-0.029104750	-1.794213980	-0.984301120
C	-2.704068750	0.080721020	0.034038880
H	-2.538952750	1.994936020	1.017475880
H	-2.475013750	-1.831670980	-0.942464120
B	-4.296001750	0.051377020	0.031712880
C	-5.003150750	-1.346604980	0.173455880
C	-5.979320750	-1.761143980	-0.777734120
C	-4.676367750	-2.243311980	1.226524880
C	-6.559700750	-3.027495980	-0.673726120
C	-5.308392750	-3.487373980	1.312034880
C	-6.247955750	-3.906277980	0.368143880
H	-7.286772750	-3.334185980	-1.423150120
H	-5.063697750	-4.147273980	2.142373880
C	-5.058386750	1.418633020	-0.112578120
C	-6.079366750	1.779856020	0.815060880
C	-4.743780750	2.341672020	-1.146809120
C	-6.708281750	3.022160020	0.710223880
C	-5.424583750	3.559871020	-1.234376120
C	-6.400700750	3.929989020	-0.308033120
H	-7.472645750	3.286252020	1.438395880
H	-5.190297750	4.236810020	-2.053956120
C	-3.678807750	-1.894969980	2.317447880
H	-2.648711750	-2.125728980	2.018129880
H	-3.702822750	-0.835682980	2.591963880
H	-3.887639750	-2.470865980	3.224714880
C	-6.409093750	-0.883115980	-1.937468120
H	-5.560860750	-0.544298980	-2.543683120
H	-7.085190750	-1.430015980	-2.601501120
H	-6.932096750	0.015012020	-1.593750120
C	-6.930796750	-5.247526980	0.482592880
H	-6.376775750	-5.926281980	1.138618880
H	-7.941406750	-5.140947980	0.898275880

H	-7.036067750	-5.728453980	-0.496147120	H	-3.971048750	2.576214020	-3.149409120
C	-6.511377750	0.869577020	1.948712880	C	-7.098835750	5.265218020	-0.393377120
H	-6.983092750	-0.045774980	1.577673880	H	-6.690733750	5.971220020	0.342006880
H	-5.671269750	0.560539020	2.581301880	H	-6.982046750	5.717528020	-1.383074120
H	-7.232934750	1.379604020	2.593944880	H	-8.170475750	5.170651020	-0.186151120
C	-3.712281750	2.052043020	-2.223634120	C	3.973506940	-0.600739650	-0.373810700
H	-2.711159750	2.392215020	-1.929977120	C	4.540632790	0.421147920	-1.376663670
H	-3.632440750	0.987852020	-2.463664120	N	4.962883760	1.181989660	-2.123333290

Cartesian coordinates for the calculated structure of 3-B-CN^-

Energy = -1760.71823159 a. u.

C	-10.455460000	-0.655356000	1.092885000	C	-4.096522000	0.091672000	-0.592030000
C	-10.169472000	-0.123218000	-0.142860000	C	-5.071595000	-0.384699000	0.497215000
C	-8.827861000	0.063569000	-0.568492000	C	-4.890550000	0.460991000	1.784592000
C	-7.749063000	-0.311488000	0.310804000	C	-4.884349000	-1.902317000	0.758207000
C	-8.086399000	-0.858662000	1.582045000	C	-2.701370000	0.112914000	-0.594794000
C	-9.400162000	-1.024824000	1.959522000	C	-1.866950000	-0.331946000	0.430581000
C	-8.542141000	0.614694000	-1.846785000	C	-4.227673000	1.066043000	-2.874907000
C	-7.252024000	0.806676000	-2.283454000	H	-11.486097000	-0.792805000	1.406177000
C	-6.207812000	0.434178000	-1.412503000	H	-10.972031000	0.164637000	-0.817397000
C	-6.423187000	-0.105842000	-0.157800000	H	-7.301582000	-1.150611000	2.269622000
N	-4.817903000	0.540023000	-1.650663000	H	-9.628884000	-1.444366000	2.935152000

H	-9.373657000	0.889497000	-2.489994000
H	-7.062450000	1.230923000	-3.263071000
H	-5.642044000	0.189072000	2.529552000
H	-3.903427000	0.311121000	2.228559000
H	-5.005866000	1.527121000	1.566437000
H	-4.986870000	-2.470135000	-0.171650000
H	-5.641768000	-2.265507000	1.456839000
H	-3.900867000	-2.120078000	1.181649000
H	-2.224477000	0.518386000	-1.480431000
H	-2.328300000	-0.748831000	1.320693000
H	-5.016715000	1.320713000	-3.579504000
H	-3.642318000	1.966708000	-2.662618000
H	-3.576963000	0.316197000	-3.335596000
B	4.056037000	-0.202085000	0.797288000
N	4.576391000	-0.861830000	3.440865000
C	2.418510000	-0.320313000	0.645822000
C	1.589902000	-0.809076000	1.694477000
H	2.065233000	-1.192457000	2.591983000
C	0.214659000	-0.809463000	1.606693000
H	-0.382053000	-1.200568000	2.429178000
C	-0.455722000	-0.307017000	0.454344000
C	0.359493000	0.201062000	-0.600302000
H	-0.102339000	0.605564000	-1.497057000
C	1.729936000	0.198610000	-0.492997000
H	2.313035000	0.625907000	-1.300660000
C	4.374941000	-0.523402000	2.342998000
C	4.326501000	1.397406000	0.366340000
C	4.077253000	2.465456000	1.278957000
C	4.300510000	3.797411000	0.905085000
H	4.112160000	4.582384000	1.636563000
C	4.738718000	4.154239000	-0.368373000
C	4.917858000	3.120995000	-1.285642000
H	5.225766000	3.366199000	-2.301691000
C	4.716627000	1.773646000	-0.953594000
C	3.552500000	2.261153000	2.687912000
H	3.241701000	3.221451000	3.114509000
H	4.302306000	1.823894000	3.353366000
H	2.687492000	1.591638000	2.717018000
C	5.006597000	5.594056000	-0.738217000
H	4.841899000	5.772115000	-1.807178000
H	6.045777000	5.877977000	-0.520829000
H	4.362363000	6.280581000	-0.176800000

C	4.960734000	0.790570000	-2.087493000
H	4.911499000	1.313402000	-3.049955000
H	4.242214000	-0.031298000	-2.112626000
H	5.948044000	0.321618000	-2.016230000
C	5.024407000	-1.330825000	0.031243000
C	4.562809000	-2.488466000	-0.646289000
C	5.466648000	-3.394494000	-1.224268000
H	5.071074000	-4.266431000	-1.744115000
C	6.845395000	-3.225228000	-1.149485000
C	7.306061000	-2.107563000	-0.454292000
H	8.379838000	-1.950510000	-0.358638000
C	6.439839000	-1.179515000	0.135706000
C	3.096930000	-2.848682000	-0.802077000
H	2.998165000	-3.838533000	-1.261435000
H	2.551005000	-2.142279000	-1.438477000
H	2.573681000	-2.882444000	0.158682000
C	7.801943000	-4.226086000	-1.755039000
H	8.656446000	-3.730232000	-2.231123000
H	7.307454000	-4.844772000	-2.512313000
H	8.210183000	-4.905873000	-0.994297000
C	7.098441000	-0.032554000	0.879492000
H	8.184429000	-0.173314000	0.905973000
H	6.746104000	0.034863000	1.912952000
H	6.897858000	0.936318000	0.411561000